(12) UK Patent Application (19) GB (11) 2 152 223 A

(43) Application published 31 Jul 1985

(21) Application No 8428518

(22) Date of filing 12 Nov 1984

(30) Priority data
(31) 654123 (32) 28 Nov 1983 (33) US

(71) Applicant
Fusion Semiconductor Systems (USA–Maryland),
7600 Standish Place, Rockville, Maryland 20855,
United States of America

(72) Inventor
John C Matthews

(74) Agent and/or Address for Service
Lloyd Wise Tregear & Co,
Norman House, 105–109 Strand, London WC2R 0AE

(51) INT CL[4]
G03C 1/52

(52) Domestic classification
G2C 1B3B 1F C14A C4A C4C2B2 C4C5B
G2X N3

(56) Documents cited
GB 1577492 EP A2 0012833 US 4211834

(58) Field of search
G2C
G2X

(54) Process for imaging resist materials

(57) A process is provided for imaging a multi-layer resist structure which comprises providing a first layer of a first resist material onto a second and different resist material where the second resist material is a photosensitive material having limited sensitivity to the imaging radiation for the first layer. The first layer is exposed to imaging radiation and developed, and is exposed to ultaviolet light radiation of predominantly wavelengths of about 260 nm. and above in order to harden the first layer. The second resist material is exposed to radiation at wavelengths of 250 nm and below, and developed.

GB 2 152 223 A

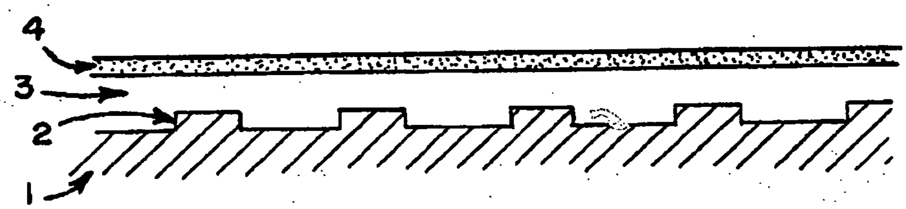

FIG.1

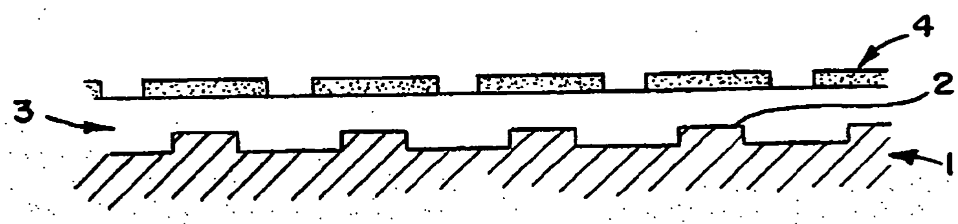

FIG.2

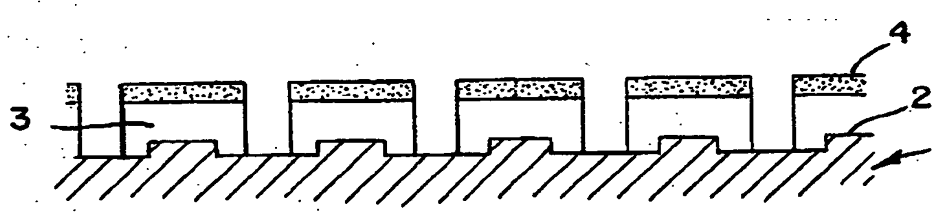

FIG.3

SPECIFICATION

Technical field

The present invention is concerned with providing an image, and is particularly concerned with providing an image or mask of a multi-layer resist article. The present invention is especially concerned with providing what is referred to as photosensitive conformable masks whereby the top layer can be rendered capable of withstanding the relatively high temperatures and the hostile environments in a reactive ion etching, planar plasma etching and ion implantation.

Background

In the manufacture of patterned devices such as semiconductor chips and carriers, the steps of etching different layers which constitute the desired product are among the most critical and crucial steps involved. In order to etch a desired pattern, the surface to be etched can be covered with a suitable mask and then the surface etched either employing a wet chemical system or a so-called dry process to etch the surface while leaving the mask intact. As the lines and spaces to be etched become smaller, such as at about 1 micron, the photolithographic procedures for producing the photoresist pattern that is the etch mask and especially the "dry processes" are affected by such parameters as reflections from the surface grain structure of the metals or polysilicon substrate to be etched, standing wave effects, variations in the photosensitive material thickness, reflections from steps and diffraction effects.

One technique for overcoming the problems of surface topology, reflections and diffractions, is to employ a multi-layer resist system known as a portable conformable mask (PCM) system. Such is described by Burn Jeng Lin, "Deep U.V. Lithography", Journal of Vacuum Science and Technology, Vol. 12, No. 6, Nov.-Dec. 1975, disclosure of which is incorporated herein by reference. The simplest multi-layer resist system employs a two-layer resist system which avoids the cost and complexity of most other multilayer systems. The bottom layer is insensitive to the radiation used to image the top resist layer, and is preferably a resist from a polymer of methyl methacrylate, preferably polymethylmethacrylate (PMMA), that is applied over the wafer topology to provide a planar surface. The top layer is generally a relatively thin (e.g., less than about 1 micron) layer of a material that is simultaneously sensitive to the imaging radiation – electron beam, X-ray, or optical radiation – and opaque to the radiation used to expose the bottom layer. Typically this can be a positive photosensitive material that responds to the imaging radiation such as ultraviolet light used in step-and-repeat photolithography and is opaque to deep U.V. wavelengths used to expose PMMA. After the top layer is imaged and developed, the bottom layer is imaged by flood exposure through the top layer resist mask and developed using, for instance deep U.V. (about 190 nm to about 250 nm).

Next, the substrate is etched. Anisotropic dry etching techniques such as reactive ion etching (RIE) or planar plasma etching (PPE) are used to avoid the undercut and resultant line width reduction, characteristic of isotropic etching methods. However, one problem associated with the anisotropic dry etching techniques is that they subject the etch mask to temperatures that exceed the plastic flow temperatures of common positive photoresists.

This problem to withstand the conditions and environment of anisotropic dry etching is present with the above-discussed portable conformable masks. Moreover, such problem is also true for many positive photosensitive materials as well as negative photosensitive materials. A positive photosensitive material is one which, on exposure to imaging radiation, is capable of being rendered soluble in a solvent in which the unexposed resist is not soluble. A negative resist material is one which is capable of polymerizing and insolublizing upon exposure to imaging radiation.

Summary of the Invention

The present invention provides a process for improving the resistance of a multi-layer resist article without a concomitant dimensional distortion of the images produced. In particular, the present invention provides a process for improving the resistance of the multi-layer resist article to anisotropic RIE and PPE environments.

The process of the present invention is concerned with providing an image which comprises providing a first layer of a first resist material onto a second and different resist material. The second resist material is a photosensitive material having limited sensitivity to the imaging radiation for the first layer such as light of wavelengths above 250 nm. The first layer is exposed to imaging radiation and developed to provide the desired image. After development, the first layer is exposed to ultraviolet light radiation of predominantly wavelengths of above about 260 nm for a time sufficient to harden the first layer. This second step for hardening the first layer does not significantly affect the structure of the underlying second layer of resist material. The second and different resist material is exposed to radiation at wavelengths of about 250 nm and below.

Summary of the drawings

Figures 1-3 are cross-sections of a substrate in various stages of fabrication in accordance with the process of the present invention.

Best and Various Modes for Carrying Out the Invention

The first layer of the first resist material employed in accordance with the present invention can be a positive or negative resist material, but preferably it is a positive resist material which, upon exposure to wavelengths of 260 nm. and above, can be hardened or cross-linked. Examples of discussions of the use of deep U.V. radiation to harden, cure or cross-link positive resists can be found in Yen et al, *Deee U.V. and Plasma Hardeninq of Photoresist Patterns*, Integrated Circuit Laboratory, Xerox, Palo Alto Research Center, Palo Alto, California; Hiraoaka et al, *High* Temperature Flow Resistance of Micron Sized Images in AZ *Resists*, AZ Resists, Volume 128, Number 12, Pages 2645-2647; and, Ma, *Plasma Resist Image Stabilization Technique (PRIST) Update*, Volume 333, Submicron Lithography, 1982, pages 1-23, disclosures of which are incorporated herein by reference.

Among those photosensitive materials found to be especially suitable are the positive photosensitive materials which are cross-linkable when exposed to U.V. radiation of 260 nm and above, and particularly those photosensitive materials sensitized with diazo compounds. Examples of such diazo sensitizers are discussed on pages 48-55 of DeForest *Photoresist Materials and Processes*, McGraw-Hill Book Company, 1975, disclosure of which is incorporated herein by reference. Some diazo compounds are benzoquinone 1, 2-diazide-4-sulphochloride; 2-diazo-1-naphthol-5-sulphonic acid ester; napthoquinone-1, 2-diazide-5-sulphochloride; napthoquinone-1, 2-diazide-4 sulphochloride; napthoquinone-2-1-diazide-4-sulphochloride; and napthoquinone 2, 1-diazide-5-sulphochloride.

The preferred photosensitive materials employed as the first layer are the phenolic-formaldehyde type novalak type polymers sensitized with a diazo compound. The phenols include phenol and substituted phenols such as cresol. A particular example of such is Shipley AZ 1350 which is an m-cresol-formaldehyde novalak polymer composition. Such a positive resist composition includes therein a diazoketone, such as 2-diazo-1-napthol-sulphonic acid ester. The composition usually contains on the order of about 158 by weight or so of the diazoketone compound. Examples of some other commercially available photosensitive materials suitable for providing the first layer of material employed in accordance with the present invention are AZ 1370 and AZ 1470 from Shipley; AZ 4110 and AZ 4210 from AZ Photoresistive Division of American Hoechst; HPR 204 from Phillip A. Hunt; and, Kodak 920 from Kodak, and OFPR 800 from Tokyo Ohka.

In addition, discussion of various photosensitive materials can be found, for instance, in the *Journal of the Electrochemical Society*, Volume 125, Number 3, March 1980, Deckert et al, "Microlithography—Key to Solid-State Fabrication", pages 45C-56C, disclosure of which is incorporated herein by reference.

The first or top layer is usually about 2,000 to about 40,000 Angstroms thick and preferably about 5,000 to about 12,000 Angstroms thick.

The second and different resist material employed in accordance with the process of the present invention, must have limited sensitivity to the imaging radiation for the first layer and preferably limited sensitivity to ultraviolet light radiation of wavelengths above 260 nm and is preferably a positive photosensitive material and most preferably, a polymer of methylmethacrylate. The most preferred photosensitive material for the second layer is polymethylmethacrylate. However, copolymers of methylmethacrylate which do not greatly increase the polymer sensitivity to wavelengths above 260 nm are also preferred in accorLance with the process of the present invention. Such materials are described by ×ayne M. Moreau, "State of the Art of Acrylate Resists, an Overview of Polymer Structure and Lithographic Performance", Optical Engineering 22 (2), March-April, 1983, disclosure of which is incorporated herein by reference. The particular thickness of the second layer must be such as to planarize the substrate and accordingly, should exceed the step height of the circuit on the substrate. This is usually about 0.2 to about 2.0 microns, and preferably about 0.5 to about 1.5 microns.

Providing the first layer on top of the second layer and the second layer on top of a substrate can be carried out in accordance with any of the known coating techniques such as spinning the polymers onto the desired surface.

The first layer is exposed to imaging radiation and developed as in single layer resist processes. In the case of the preferred positive photosensitive materials discussed hereinabove, the resist image is typically produced using a projection mask aligner, and development with removal of the exposed portion with an aqueous alkaline solution.

The developed first layer is hardened or cross-linked by exposure to ultraviolet light radiation having wavelengths predominantly above about 260 nm and preferably from about 260 nm to about 320 nm. In addition, it is preferred that the ratio of wavelengths from 260-320 nm to those less than 260 nm is greater than about 10: 1.

The exposure is continued for a time sufficient to harden or cross-link the first layer and is usually about 5 seconds to about 15 minutes, and preferably about 15 seconds to about 90 seconds.

In addition, if desired, the first layer can be subjected to a hard bake by heating at elevated temperatures above 100°C and preferably at about 120° to about 200°C either during and/or after the exposure to the ultraviolet light radiation of wavelengths above 260 nm. The maximum temperature should be lower than that which would cause the second layer to distort. If desired, the technique of exposing the resist to radiation while subjecting it to elevated temperature upon increase in the degree of polymerization, due to the exposure to the U.V. radiation, while maintaining the elevated temperature below the flow temperature of the film, as disclosed in co-pending U. S. Patent Application Serial No. 497,466, can be employed herein, and accordingly, the disclosure of said application Serial No. 497,466 is incorporated herein by reference. In particular, such procedure significantly reduces the necessary exposure time. As discussed therein, the resist material, during the exposure to the U.V. radiation, is heated to an elevated temperature which is greater than the flow temperature of the resist material at the start of the exposure to the U.V. radiation. If desired, the thermal chuck described in U.S. Patent Application Serial No. 497,466 can be employed in accordance with the present invention.

The dosage of the U.V. radiation of wavelength of 260-320 nm in accordance with the present invention to the resist material is at least about 1 Joule/cm^2 and preferably about 2 Joule/cm^2.

The exposure to the radiation of a wavelength of 260 nm to 320 nm can be achieved by employing a mercury lamp source and a quartz envelope to attentuate wavelengths below 250 nm. A suitable quartz envelope is made from ozone free quartz, and is commercially available such as under the trade designation GE219 Quartz from General Electric and M-84 Quartz from Heraeus Amersil. In addition, although certainly not necessary, the preferred U.V. radiation having wavelengths of 260 nm to 320 nm are highly non-collimated. The exposure to wavelengths above 260 nm is carried out after development of the first layer and preferably prior to exposure of the second and different layer to deep U.V. radiation. However, if desired, the exposure to wavelengths above 260 nm can be carried out after exposure of the second layer to deep U.V. radiation and can be carried out before or after the development of the second and different layer.

The second and different layer of resist material is exposed to radiation capable of depolymerizing the photosensitive material of the second layer. For instance, in the case of polymers of methylmethacrylate, the radiation employed is in the deep U.V. range such as at about 190 nm. to about 250 nm. The exposed photosensitive material can then be developed by dissolving in a ketone type solvent, such as methylisobutylketone, or in an aromatic solvent such chlorobenzene without dissolving the hardened top layer.

The structure is now capable of withstanding the conditions of RIE or PPE of alumninum and alloys thereof without excessive erosion of the mask.

Reference to the Figures further illustrates the present invention. Figure 1 illustrates a substrate 1 containing steps or profile 2. On top of substrate 1 is a layer of resist material such as polymethylmethacrylate 3 for planarization. A layer of resist material 4 is provided on top of layer 3. The top layer 4 is exposed to imaging radiation and then developed to provide the structure shown in Figure 2. Next, the structure is subjected to U.V. radiation having predominantly 260 nm to 320 nm wavelength and insignificant amounts of energy below 250 nm whereby the remainder of layer 4 is cross-linked and hardened and the underlying layer 3 is not significantly effected. Next, the structure is subjected to deep U.V. radiation of about 190 to about 250 nm followed by development with a ketone such as methylisobutylketone or aromatic compound such as chlorobenzene, to provide the structure shown in Figure 3.

After this, the structure can be subjected to reactive ion etching and the mask will withstand the temperature and environment of the etching.

The following non-limiting example is presented to further illustrate the present invention.

Example

A 100 mm silicon wafer containing a bilayer resist structure containing a previously patterned or imaged 0.5 micron top layer of Kodak 809 resist on top of a 1.5 micron planarized layer of PMMA is exposed to stabilizing U.V. radiation emitted from bulbs constructed of M-84 Quartz from Heraeus-Amersil in a Microlite 126 PM photostabilizer produced by Fusion Semiconductor Systems Corporation. The characteristic spectrum emitted from this source has a ratio of radiation in the wavelength range 260 nm to 320 nm to radiation below 260 nm in excess of 100 to 1. The temperature of the wafer is linearly increased from a starting temperature of 50°C to an ending temperature of 185°C during a 2 minute exposure to the above source using a thermal chuck of the type disclosed in U.S. patent application S.N. 497,466. Microscopic examination of the resist structure after this exposure shows no evidence of resist flow or image distortion. Subsequent analysis by scanning electron microscope (SEM) confirms that the resist image is dimensionally stable.

The wafer with the stabilized bilayer structure produced as described above is next exposed to deep U.V. illumination from a

Microlite 100 M Illuminator produced by Fusion Semiconductor Systems and developed in methylisobutyl ketone (MIBK). During the 45 second MIBK development cycle the stabilized Kodak 809 resist layer is not removed and the exposed PMMA is cleanly developed. The resulting bilayer resist structure is examined by optical microscopy and SEM. The Kodak 809 resist image held its line width and edge profile and the PMMA structure shows the high contrast image characteristic of the bilayer resist process without stabilizing radiation.

CLAIMS

1. A process for providing an image which comprises:

(a) providinq a first layer of a first resist material onto a second and different resist material which is a photosensitive material having limited sensitivity to the imaging radiation for the first resist material;

(b) exposing said first layer to imaging radiation and developing said first layer thereby providing a resist image mask;

(c) exposing said first layer to ultraviolet light radiation of wavelength of at least about 260 nm for a time sufficient to harden said first layer;

(d) exposing said second and different resist material to imaging radiation at wavelengths of 250 nm and below through the first resist image mask and;

(e) developing said second and different resist layer.

2. The process of claim 1 wherein the first layer is exposed, in step (c), to ultraviolet light radiation of wavelengths of about 260 nm to about 320 nm.

3. The process of claim 1 wherein the ratio of wavelengths of ultraviolet light radiation employed in step (c) which is greater than 260 nm to wavelengths less than 260 nm is at least 10:1.

4. The process of claim 1 wherein said second and different resist layer is exposed to actinic radiation subsequent to step (c).

5. The process of claim 1 wherein the exposing of said first layer in step (c) is about 5 seconds to about 15 minutes.

6. The process of claim 1 wherein the exposing of said first layer in step (c) is about 15 seconds to about 90 seconds.

7. The process of claim 1 wherein said first layer is subjected to elevated temperatures above 100°C during or after the exposing to ultraviolet light radiation in step (c), or both.

8. The process of claim 7 wherein said elevated temperature is about 120 to about 200°C.

9. The process of claim 1 which further includes subjecting the structure to reactive ion etching or PPE after development of the second and different resist layer.

10. The process of claim 1 wherein the exposing of said first layer to ultraviolet light radiation in step (c) is highly non-collimated light.

11. The process of claim 1 wherein the second and different resist material is exposed to radiation of wavelengths of about 190 nm to about 250 nm.

12. The process of claim 1 wherein said second and different resist layer is from a polymer of methylmethacrylate.

13. The process of claim 1 wherein said first resist material is a diazo sensitized polymer composition.

14. The process of claim 13 wherein said polymer is a phenolic-formaldehyde novalak type polymer.

15. The process of claim 1 wherein said first layer is about 2000 to about 40,000 angstroms thick.

16. The process of claim 1 wherein said first layer is about 5000 to about 12,000 angstroms thick.

17. The process of claim 1 wherein said second and different resist layer is developed subsequent to step (c).

18. The process of claim 17 wherein said second and different resist layer is exposed prior to step (c).

19. The process of claim 1 wherein said second and different resist layer is exposed subsequent to step (c).

20. The process of claim 1 wherein said second and different resist layer is developed prior to step (c).

21. A process for providing an image on a substrate using a first layer of resist material over a second layer of resist material substantially as described in the specific example.

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